

UNCLASSIFIED

AD 258 410

*Reproduced
by the*

**ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA**



UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

ALSTIA 25864-103 ALSTIA
CATALOGED BY HS

AERONUTRONIC

A DIVISION OF

Ford Motor Company.

\$2.60

RESEARCH LABORATORIES

TECHNICAL REPORT

AN EXPERIMENTAL PROGRAM FOR OBTAINING
THE THERMODYNAMIC PROPERTIES OF PROPELLANT
COMBUSTION PRODUCTS

FINAL REPORT

61-3-5

XEROX

Prepared for

Bureau of Naval Weapons
Department of the Navy
Washington 25, D C

Under Contract

NOrd 17980, Task 3 (C)
ARPA Order 22-59, Task 4 (c)
Work on this program is being
continued under Contract N0W 61-0905 (ARPA)

Prepared by

D L Hildenbrand
L P Theard

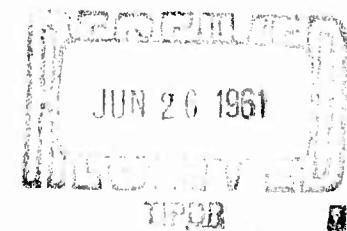
15 June 1961

AERONUTRONIC

A DIVISION OF *Ford Motor Company*

FORD ROAD / NEWPORT BEACH, CALIFORNIA

ASTIA



SUMMARY

Torsion-effusion studies of the vaporization of zirconium tetrafluoride have been completed. The results yield a condensation coefficient of about 0.08 and a heat of sublimation of 55.8 kcal/mole at 298°K, in agreement with tentative data reported earlier. A vapor molecular weight of 161 ± 12 has been obtained from combined torsion and weight loss measurements (monomer = 167.2), indicating the saturated vapor to be highly monomeric. From these results, the heat of formation of $ZrF_4(g)$ at 298°K is derived as -401.1 ± 3 kcal/mole. Studies of the vaporization of ZrF_4 in the presence of finely divided elemental zirconium indicate that lower fluorides are not formed under these conditions.

The vapor pressures of aluminum trifluoride and a 1:1 mole ratio mixture of lithium and aluminum fluorides have been measured by the torsion-effusion method. A heat of sublimation at 298°K of 71.0 ± 0.5 kcal/mole is obtained for AlF_3 , from which the heat of formation of $AlF_3(g)$ at 298°K is derived as -285.3 ± 2 kcal/mole. Measurements on the $LiF-AlF_3$ mixture indicate congruent vaporization to a stable $LiAlF_4$ gaseous molecule, for which the heat of formation at 298°K is derived as -447 ± 7 kcal/mole.

Measurements of the dissociation pressure of aluminum nitride are in progress. Results to date indicate a condensation coefficient of about 2×10^{-3} and a heat of formation at 298°K of about -73 kcal/mole for crystalline AlN . The latter is in agreement with recent values obtained by reaction calorimetry.



AERONUTRONIC

A DIVISION OF *Ford Motor Company*

The vaporization of magnesium nitride has been studied over the range 1100 to 1260°K by the torsion method. From the variation of pressure with orifice size, a condensation coefficient of about 5×10^{-3} is indicated. However, the derived equilibrium pressures are lower by a factor of ten than pressures calculated assuming decomposition to the gaseous elements. The latter suggests that the accepted value of the heat of formation of crystalline Mg_3N_2 may be in error, or that surface effects are limiting the rate of vaporization.

Boron oxyfluoride monomer and trimer ions have been identified as major species in the mass spectrum of the vapor effusing from a Knudsen cell containing a mixture of magnesium fluoride and boric oxide. Positive identification of the $(OBF)^+$ and $(OBF)_3^+$ ions was made through the observed isotopic distribution of mass peaks.

Exploratory specific heat measurements on tantalum and platinum in the range below 1500°K have indicated that satisfactory results can be obtained by the radiation-cooling rate method. Measurements on powdered samples indicate that, as expected, poor heat transfer within the powders will be a serious problem.



AERONUTRONIC

A DIVISION OF Ford Motor Company

CONTENTS

SECTION	PAGE
1 INTRODUCTION	1
2 EFFUSION STUDIES	
2.1 The Vaporization of Zirconium Tetrafluoride	2
2.2 The Vaporization of Aluminum Trifluoride and Lithium Aluminum Fluoride Mixtures	7
2.3 The Vaporization of Aluminum Nitride	12
2.4 The Vaporization of Magnesium Nitride	13
3 TRANSPIRATION STUDIES	17
4 MASS SPECTROMETRY	
4.1 Vapor Species in the Boron-Oxygen-Fluorine System	18
5 SPECIFIC HEAT MEASUREMENT	22
6 FUTURE PROGRAM	23
REFERENCES	24



AERONUTRONIC

A DIVISION OF *Ford Motor Company*

ILLUSTRATIONS

FIGURE	PAGE
1 ZrF ₄ Equilibrium Pressure Data	5
2 Vapor Pressures in the LiF-AlF ₃ System.	9
3 Magnesium Nitride Dissociation Pressure Data. . . .	15



AERONUTRONIC

A DIVISION OF *Ford Motor Company*.

TABLES

NUMBER	PAGE
I Torsion Vapor Pressure of ZrF ₄	3
II Equilibrium Pressure and Heat of the Reaction ZrF ₄ (s) = ZrF ₄ (g)	6
III The Vapor Molecular Weight of ZrF ₄	6
IV The Vapor Pressure and Heat of Sublimation of AlF ₃	8
V The Torsion Vapor Pressure of a LiF-AlF ₃ 1:1 Mole Ratio Mixture.	11
VI Magnesium Nitride Dissociation Pressure Data	14
VII Mass Spectrum of Vapor Species from 1:1 Mixture of MgF ₂ and B ₂ O ₃ at 995 °C.	20



AERONUTRONIC

AERONUTRONIC

A DIVISION OF *Ford Motor Company*

SECTION 1

INTRODUCTION

The studies reported here are part of an experimental program which is designed to provide thermodynamic data required in the analysis of propulsion systems. Specific areas of study are the thermodynamics of vaporization of light metal compounds and the specific heats of condensed phases. Vaporization data, from which heats and free energies of formation of important species can be derived, are being obtained by effusion, transpiration and mass spectrometric techniques. A method is under development for determination of specific heats from measurement of vacuum cooling rates.

The results of some of these studies are described in the following sections.

SECTION 2

EFFUSION STUDIES

2.1 THE VAPORIZATION OF ZIRCONIUM TETRAFLUORIDE

Vapor pressure data for crystalline ZrF_4 given in the previous report¹ were shown to be dependent on effusion orifice size, but were not extensive enough to permit reliable extrapolation to zero hole area so as to obtain equilibrium pressure data. Additional torsion vapor pressure data have been obtained with another graphite cell of intermediate orifice size, using the same sample and technique of measurement as described previously,^{1,2,3} and are given in Table I. The torsion pressure data were computed from the relation

$$P_T = \frac{2k\theta}{\sum afq} \quad (1)$$

where P_T is the pressure, k is the torsion constant of the suspension system, θ is the angular deflection and a , f and q are the area, force factor and moment arm of each of the effusion orifices. When the data of Table I are compared with the data of Table VI, reference (1), it is apparent that a low condensation coefficient is effecting a departure from equilibrium. It has been shown¹ that equilibrium and observed pressures are related to cell geometry through the expression

$$P_e = P_T \left(1 + \frac{Ca}{\alpha A}\right) \quad (2)$$

where P_e is the equilibrium pressure, P_T is the observed torsion pressure, C is the orifice Clausing factor, a is the orifice area,

AERONUTRONIC

AERONUTRONIC

A DIVISION OF *Ford Motor Company*

TABLE I

TORSION VAPOR PRESSURE OF ZrF_4

Cell No. 9

<u>T^0_K</u>	<u>$P_T \times 10^5, \text{ atm}$</u>
710.9	0.06
734.5	0.104
754.6	0.260
765.6	0.388
772.5	0.541
780.5	0.800
795.0	1.42
803.3	1.95
811.9	2.72
819.0	3.53
824.9	4.36

$$\bar{a} = 0.0120 \text{ cm}^2$$

$$\bar{c} = 0.80$$

$$\Sigma afq = 0.02255 \text{ cm}^3$$

$$k = 3.12 \text{ dyne cm/rad}$$

α is the condensation coefficient and A is the effective vaporizing surface area. If the data obtained with graphite cells 6, 7 and 9 (the three smallest orifices) are treated according to equation (2), a smooth extrapolation to zero hole size can be made. From the slope of such a plot, an α value of 0.08 is obtained, provided the effective vaporizing surface is taken as the cell cross sectional area. An α so obtained is in all likelihood an upper limit to the true value. The data obtained with graphite cell 8 (largest orifices)¹ do not correlate well with the others when treated by equation (2), and indicate that vapor is apparently withdrawn at too high a rate to maintain the required steady state pressure.

Ratios of P_e/P_T were computed for each of the effusion cells from equation (2), using α and the appropriate geometrical factors, and were then used to compute equilibrium pressures from the observed values. Equilibrium pressure data obtained in this way are shown in Figure 1, from which it is apparent that treatment according to equation (2) brings the results of all three cells into good overall agreement. Figure 1 also shows the results to be in good agreement with the data of Cantor et al.⁴ and to differ considerably from the results of Sense et al.⁵, both sets extrapolated from data at higher temperatures.

The equilibrium pressure data and derived thermodynamic properties are summarized in Table II. Free energy functions have been estimated as described in reference (1). An average third law heat of sublimation at 298 °K of 58.0 ± 0.2 kcal/mole is derived, as compared to a second law value of 53.5 kcal/mole. The discrepancy between the two values could well arise from error in the estimated free energy functions; for the present, an average value of 55.8 ± 3 kcal/mole is adopted. Combining this value with the heat of formation of crystalline ZrF_4 at 298 °K, -456.9 kcal/mole⁶, one derives the heat of formation of $ZrF_4(g)$ at 298 °K as -401.1 ± 3 kcal/mole, in agreement with the earlier tentative value based on incomplete data¹. Reliable free energy functions are needed before the uncertainty can be further reduced.

The assumption of monomeric vapor is implicit in the derivation of the thermal data in Table II. In order to check the validity of this assumption, the molecular weight of the saturated vapor has been determined from combined torsion and effusion weight loss measurements, as described previously^{2,3}. From the molecular weight data summarized in Table III, it is apparent that the saturated vapor in this range is highly monomeric, justifying the original assumption.

In order to check on the stability of gaseous lower fluorides, the measurements with graphite cell 9 were repeated with a mixture of ZrF_4 and finely divided zirconium metal. The vapor pressure of this mixture was identical with that of pure ZrF_4 , indicating that gaseous sub-halides are not stable under these conditions.

AERONUTRONIC

AERONUTRONIC

A DIVISION OF *Ford Motor Company*

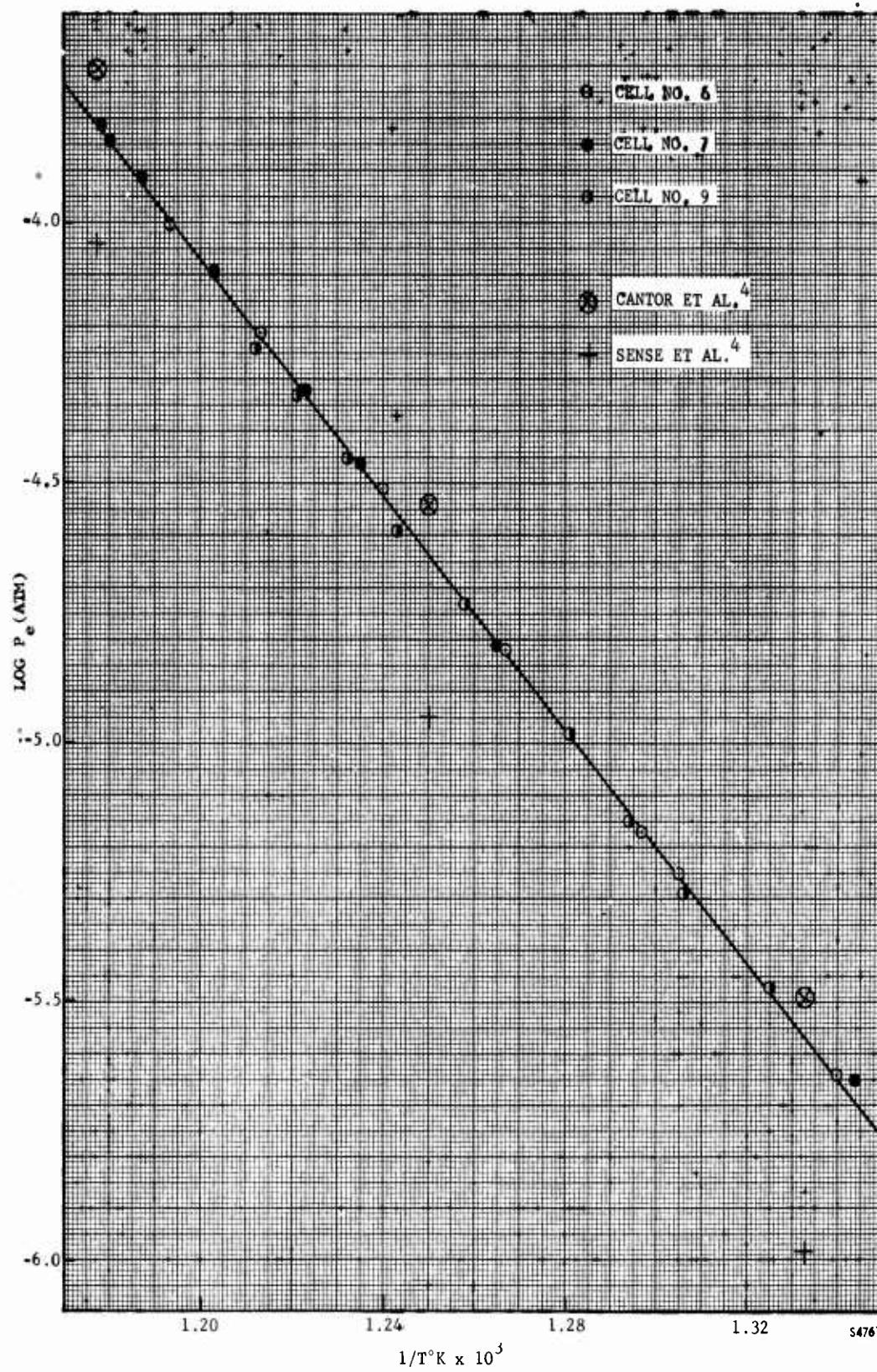


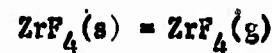
FIGURE 1. ZrF_4 EQUILIBRIUM PRESSURE DATA



AERONUTRONIC

DIVISION OF Ford Motor Company

TABLE II
EQUILIBRIUM PRESSURE AND HEAT OF THE REACTION



<u>T°K</u>	<u>P_e × 10⁵, atm</u>	<u>ΔF° / T</u>	<u>(F-H₂₉₈)_{gas} / T</u>	<u>(F-H₂₉₈)_{solid} / T</u>	<u>ΔH₂₉₈, kcal/mole</u>
750	0.263	25.5	85.0	33.6	57.8
800	2.29	21.2	86.0	34.7	58.0
850	15.8	17.4	86.9	35.7	58.2
av. 58.0 ± 0.2					

TABLE III
THE VAPOR MOLECULAR WEIGHT OF ZrF_4

<u>T°K</u>	<u>M*</u>	<u>T°K</u>	<u>M*</u>
800.3	143.5	816.4	160.7
801.3	202.5	816.4	163.0
809.3	158.6	826.5	139.0
812.4	161.5		

av. 161.2 ± 12

ZrF_4 monomer = 167.2

Graphite cell No. 6

$$\Sigma aC = 0.03585 \text{ cm}^2$$

$$M^* = \left[\frac{w}{(44.3)(P_T)(\Sigma aC)} \right]^2 T$$

2.2 THE VAPORIZATION OF ALUMINUM TRIFLUORIDE AND LITHIUM ALUMINUM FLUORIDE MIXTURES

a. Aluminum Trifluoride

Because of uncertainties in the thermodynamics of AlF_3 vapor species and because of the need for such data in the analysis of the vaporization of mixed fluorides, the vapor pressure of crystalline AlF_3 has been measured by the torsion method over the range 990 to 1100°K. A high purity sample was prepared by dehydration of Baker and Adamson reagent grade material at 500 °C in a stream of anhydrous HF. Results obtained with three different graphite effusion cells are given in Table IV along with derived third law heats of sublimation. The results obtained with each cell were quite reproducible, but showed the pressures of cell 7 (smallest orifices) to be slightly higher than the others, indicating a condensation coefficient of around 0.2. For this reason, the pressure data obtained with cell 7 were assumed to be close to equilibrium and were used in deriving thermodynamic properties. The measured torsion pressures are in good agreement with the torsion data of Witt and Barrow⁷ in absolute magnitude, but differ slightly in temperature dependence. A plot of the cell 7 vapor pressure data is given in Figure 2.

Porter and Zeller⁸ have shown by mass spectrometry that saturated AlF_3 vapor is essentially monomeric. It is planned to check this point by torsion-Knudsen measurements. Table IV gives the derived third law heat of the sublimation process



as 71.2 ± 0.2 kcal/mole at 298 °K. Free energy functions have been taken from reference (9). The derived third law heat is in good agreement with the value 71.5 kcal/mole obtained from a third law treatment of the data of other observers based on measurements at higher temperatures¹⁰. From the temperature dependence of pressure, a second law heat of sublimation at 298 °K of 70.7 kcal/mole is calculated in good agreement with the third law value; an average value of 71.0 ± 0.5 kcal/mole is adopted. This may be taken as evidence that the estimated vibrational assignment used in computing the thermal functions of $\text{AlF}_3(\text{g})$ in reference (9) is more nearly correct than that of Witt and Barrow⁷, which leads to a third law heat that is 1.8 kcal higher. Taking $\Delta H_f^{\circ} \text{ at } 298$ for crystalline AlF_3 as -356.3 ± 2 kcal/mole⁹, one computes the heat of formation of $\text{AlF}_3(\text{g})$ at 298 °K as -285.3 ± 2 kcal/mole.

AERONUTRONIC

AERONUTRONIC

A DIVISION OF Ford Motor Company

TABLE IV

THE VAPOR PRESSURE AND HEAT OF SUBLIMATION
OF AlF_3

Cell No. 6

$T^{\circ}\text{K}$	$P_T \times 10^5, \text{atm}$
958.4	0.12
971.4	0.18
990.7	0.36
1002.4	0.52
1009.2	0.66
1020.4	0.96
1043.6	1.90
1059.5	3.00
1077.2	4.84

$$\bar{a} = 0.0210 \text{ cm}^2$$

$$\bar{c} = 0.85$$

$$\Sigma afq = 0.02045 \text{ cm}^3$$

$$k = 3.51 \text{ dyne cm/rad}$$

Cell No. 9

$T^{\circ}\text{K}$	$P_T \times 10^5, \text{atm}$
937.5	0.06
992.4	0.40
1020.2	1.01
1047.4	2.25
1062.8	3.42
1072.6	4.52
1080.4	5.43

$$\bar{a} = 0.0120 \text{ cm}^2$$

$$\bar{c} = 0.80$$

$$\Sigma afq = 0.02255$$

$$k = 3.55 \text{ dyne cm/rad}$$

Cell No. 7

$T^{\circ}\text{K}$	$P_T \times 10^5, \text{atm}$	$\frac{\Delta F}{T}$	$-\Delta \left[\frac{F-H_{298}}{T} \right]$	$\Delta H_{298}, \text{kcal/mole}$
991.7	0.46	24.4	47.3	71.2
1011.7	0.94	23.0	47.3	71.2
1034.8	1.87	21.6	47.2	71.2
1056.8	3.74	20.3	47.1	71.2
1072.6	5.92	19.4	47.1	71.3
1087.9	9.11	18.5	47.0	71.2
1097.8	12.0	17.9	47.0	71.3
1101.4	13.2	17.8	47.0	71.4

av. 71.2 ± 0.2

$$\bar{a} = 0.0053 \text{ cm}^2$$

$$\bar{c} = 0.74$$

$$\Sigma afq = 0.00928 \text{ cm}^3$$

$$k = 3.52 \text{ dyne cm/rad}$$

AERONUTRONIC

AERONUTRONIC

A DIVISION OF *Ford Motor Company*

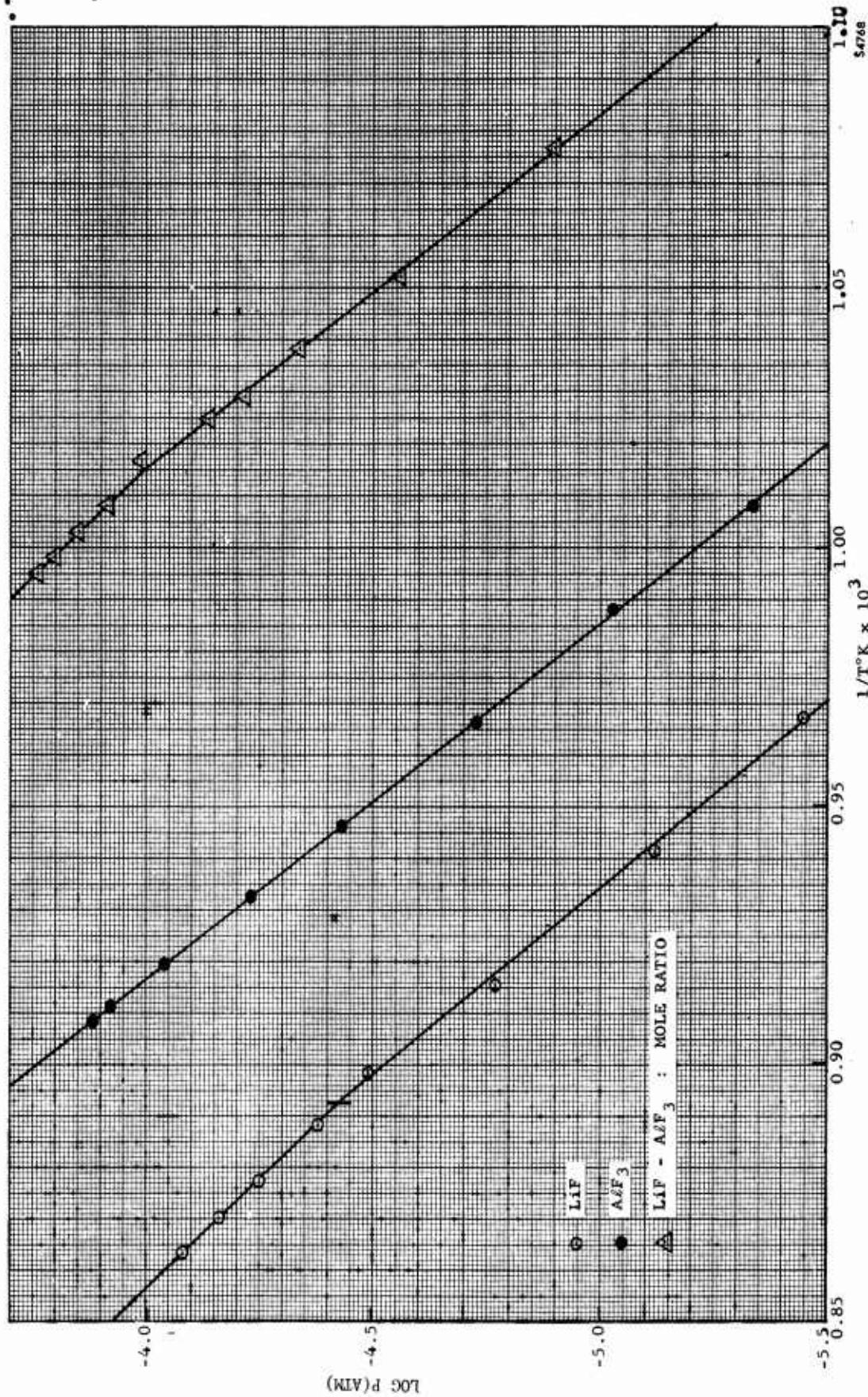


FIGURE 2. VAPOR PRESSURES IN THE LiF-AlF₃ SYSTEM

b. Lithium Aluminum Fluoride Mixtures

In order to investigate the importance of gaseous mixed metal fluorides, the vaporization of LiF - AlF₃ mixtures is being studied. The vapor pressure of a 1:1 mole ratio mixture has been measured by the torsion method over the range 900 to 1000 °K and the results are presented in Table V. A sample was made up from material previously used in measurements on the pure fluorides. As with AlF₃, the vapor pressure data obtained with cell 7 (smallest orifices) are slightly higher than the others, and are assumed to be equilibrium values. In Figure 2, the vapor pressure of the mixture is compared with the vapor pressures of pure AlF₃ and LiF, and is seen to be considerably higher than that of either of the constituent fluorides at any given temperature. Although AlF₃ is more volatile than LiF, the vapor pressure showed no change with amount of material vaporized, indicating the mixture to be undergoing congruent vaporization. Thus, the vapor must have the same composition as the condensed phase, i.e. (LiF·AlF₃)_n. Strong evidence for the existence of a lithium aluminum fluoride gaseous molecule comes from the magnitude of the vapor pressure, since only through formation of a stable gaseous mixed fluoride can the vapor pressure of the mixture greatly exceed that of either of the constituent fluorides, as it does here. Porter and Zeller⁸ have examined the mass spectrum of the saturated vapor over a 1:1 LiF-AlF₃ mixture in the same temperature range and conclude that LiAlF₄ is the major vapor species, although mixed fluoride ions were minor ionic species at the ionizing electron energies used. Until the vapor molecular weight can be checked, it is assumed that vaporization proceeds according to the process



and the data were treated as such.

From the slope of the vapor pressure plot, the heat of sublimation of LiAlF₄ at 1000 °K is calculated as 62 kcal/mole. If the heat capacities of LiF and AlF₃ are assumed to be additive in the mixed fluoride solid and vapor, $\Delta H_{\text{sub},298}$ is calculated as 67 kcal/mole. Using the entropy estimate of Porter and Zeller⁸ for LiAlF₄(g) and assuming the entropies of LiF and AlF₃ to be additive in the condensed mixture, one computes a third law heat for reaction (4) at 298 °K of 63 kcal/mole, in reasonable agreement with the second law estimate. An average value, 65 kcal/mole, is adopted.

In order to estimate $H_f^{\circ}_{298}$ for LiAlF₄(g), the heat of formation of the condensed mixed fluoride is needed. Phase equilibrium studies show that such compounds are formed in mixed fluoride systems.



AERONUTRONIC

A DIVISION OF *Ford Motor Company*

TABLE V

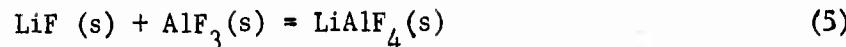
THE TORSION VAPOR PRESSURE OF A LiF-AlF₃

1:1 MOLE RATIO MIXTURE

Cell No. 7		Cell No. 9	
<u>T</u> ₀ K	<u>P</u> _T ^{x10⁵} , atm	<u>T</u> ₀ K	<u>P</u> _T ^{x10⁵} , atm
928.5	1.27	910.9	0.32
930.9	2.72	912.8	0.60
963.7	4.52	929.8	1.12
975.8	7.25	948.8	2.16
997.4	13.8	959.5	3.14
1005.4	17.3	967.8	4.12
963.5	4.15	975.1	5.41
971.8	5.96	982.4	7.05
933.4	10.3		
992.4	12.0		
1001.7	15.7		
1006.2	17.5		

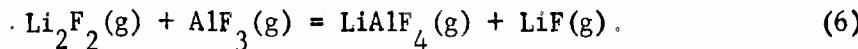
Cell constants given in Table IV

In the absence of thermal data on the LiF-AlF₃ system, the heat of solid mixed fluoride formation was estimated from data on Na₃AlF₆ as -5 kcal/mole of metal fluoride¹¹. If mixed oxide systems are used as a guide, data show that the heat of addition per mole of metal oxide remains nearly constant as the mixed oxide ratio is varied. On this basis, ΔH_{298}^0 for the reaction

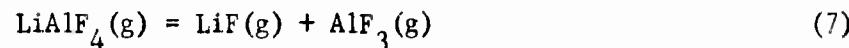


is estimated as $-10 \pm$ kcal, so that ΔH_{298}^0 for LiAlF₄(s) is taken as -512 ± 5 kcal/mole. A break in the vapor pressure curve, together with the observation that samples heated above 985 °K were fused, indicates the melting point of LiAlF₄(s) to be about 990 °K. From the estimated heat of formation of the solid and the adopted heat of sublimation, the heat of formation of LiAlF₄(g) at 298 °K is estimated as $-447 \pm$ kcal/mole. Vapor molecular constant data and solid heat and entropy data, particularly, are needed before the value can be refined.

The ΔH_{298}^0 value obtained for LiAlF₄(g) can be compared with a value obtained by Porter and Zeller⁸ from a mass spectrometric study of the gaseous equilibrium.



From a third law treatment involving the observed ion intensities, they have deduced for reaction (6) $\Delta H_{1000}^0 = -9.0 \pm$ kcal and give for the dissociation reaction



the value $\Delta H_{1000}^0 = 73 \pm 4$ kcal. The results of this research give for reaction (7) $\Delta H_{298}^0 = 81 \pm 7$ kcal. Because ΔC_p for reaction (7) is believed to be small, the two results can be compared directly. The agreement is felt to be good, considering the difference in methods.

Measurements are continuing on other LiF - AlF₃ compositions.

2.3 THE VAPORIZATION OF ALUMINUM NITRIDE

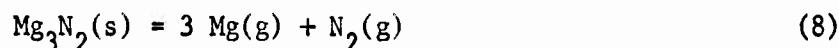
The dissociation pressure of aluminum nitride is being measured by the torsion method using graphite effusion cells. Results to date indicate a large dependence of effusion pressure on orifice size, and are consistent with a condensation coefficient of about 2×10^{-3} . This is much lower than that observed for boron nitride. From equilibrium

pressures estimated by use of equation (2), one derives the heat of formation of crystalline AlN at 298°K as -73 ± 2 kcal/mole, in fair agreement with recent reaction calorimetric values⁹.

The results will be reported in detail when measurements with all of the effusion cells are completed.

2.4 THE VAPORIZATION OF MAGNESIUM NITRIDE

As an extension of studies on other light metal nitrides, the vaporization of magnesium nitride has been studied by the torsion-effusion method over the range 1100 to 1260°K. The results are of interest in establishing trends among these compounds and will be valuable in analyzing subsequent data on beryllium nitride. A sample was prepared by heating high purity magnesium filings in a nitrogen stream, as described by Mitchell¹². The resulting brown-yellow powder had an X-ray diffraction pattern identical with that on file for pure Mg₃N₂; chemical analysis indicated the material to be better than 99 percent pure. A summary of the observed pressure (P_T) data obtained with several graphite cells of varying orifice size is given in Table VI. As with other nitrides, there is a large variation in observed pressure with hole size; the results can be correlated satisfactorily by equation (2), yielding a condensation coefficient of 5×10^{-3} . Equilibrium pressures, P_e, derived from this treatment are given in Table VI and are shown graphically in Figure 3. It is apparent that the results of all three effusion cells are brought into close agreement. However, Figure 3 also shows that the pressures so derived are lower by more than a factor of ten than pressures computed for the dissociation



using recently selected thermochemical data¹³. If the thermochemical data are correct, only complete reaction of the nitride sample with the effusion cell can produce a derived pseudo-equilibrium pressure lower than that calculated for decomposition to the elements. An examination of the samples by X-ray diffraction after completion of the measurements showed, as before, only high purity Mg₃N₂; such was expected, since magnesium does not form a stable carbide in this temperature range. Formation of a gaseous nitride molecule, or of any other molecular species, could result only in a higher pressure than that calculated for reaction (8).

The pressure data in Table VI were obtained with the resistance-heated apparatus³, employing thermocouples for temperature measurement; each set of results was completely reproducible. In order to double-check



AERONUTRONIC

A DIVISION OF *Ford Motor Company*

TABLE VI

MAGNESIUM NITRIDE DISSOCIATION PRESSURE DATA

Cell No. 3

T°K	P _T × 10 ⁵ , atm	P _e × 10 ⁵ , atm
1132.4	0.44	2.3
1163.2	1.08	5.6
1181.8	1.77	9.1
1194.7	2.50	12.9
1201.0	3.00	15.5
1207.3	3.56	18.4

$$\bar{a} = 0.0105 \text{ cm}^2$$

$$\bar{c} = 0.75$$

$$\Sigma afq = 0.01872 \text{ cm}^3$$

$$k = 3.51 \text{ dyne cm/rad}$$

Cell No. 5

T°K	P _T × 10 ⁵ , atm	P _e × 10 ⁵ , atm
1191.5	11.0	14.1
1202.3	14.2	18.2
1210.2	16.5	21.1
1216.5	19.0	24.3
1224.5	22.5	28.8

$$\bar{a} = 0.0010 \text{ cm}^2$$

$$\bar{c} = 0.54$$

$$\Sigma afq = 0.000977 \text{ cm}^3$$

$$k = 3.47 \text{ dyne cm/rad}$$

Cell No. 7

T°K	P _T × 10 ⁵ , atm	P _e × 10 ⁵ , atm
1116.4	0.42	1.3
1150.9	1.22	3.7
1170.1	2.16	6.5
1184.7	3.10	9.3
1197.1	4.22	12.6
1204.7	4.92	14.7
1210.9	5.84	17.5

Cell constants in Table IV

$$k = 3.53 \text{ dyne cm/rad}$$

AERONUTRONIC

AERONUTRONIC

DIVISION OF Ford Motor Company

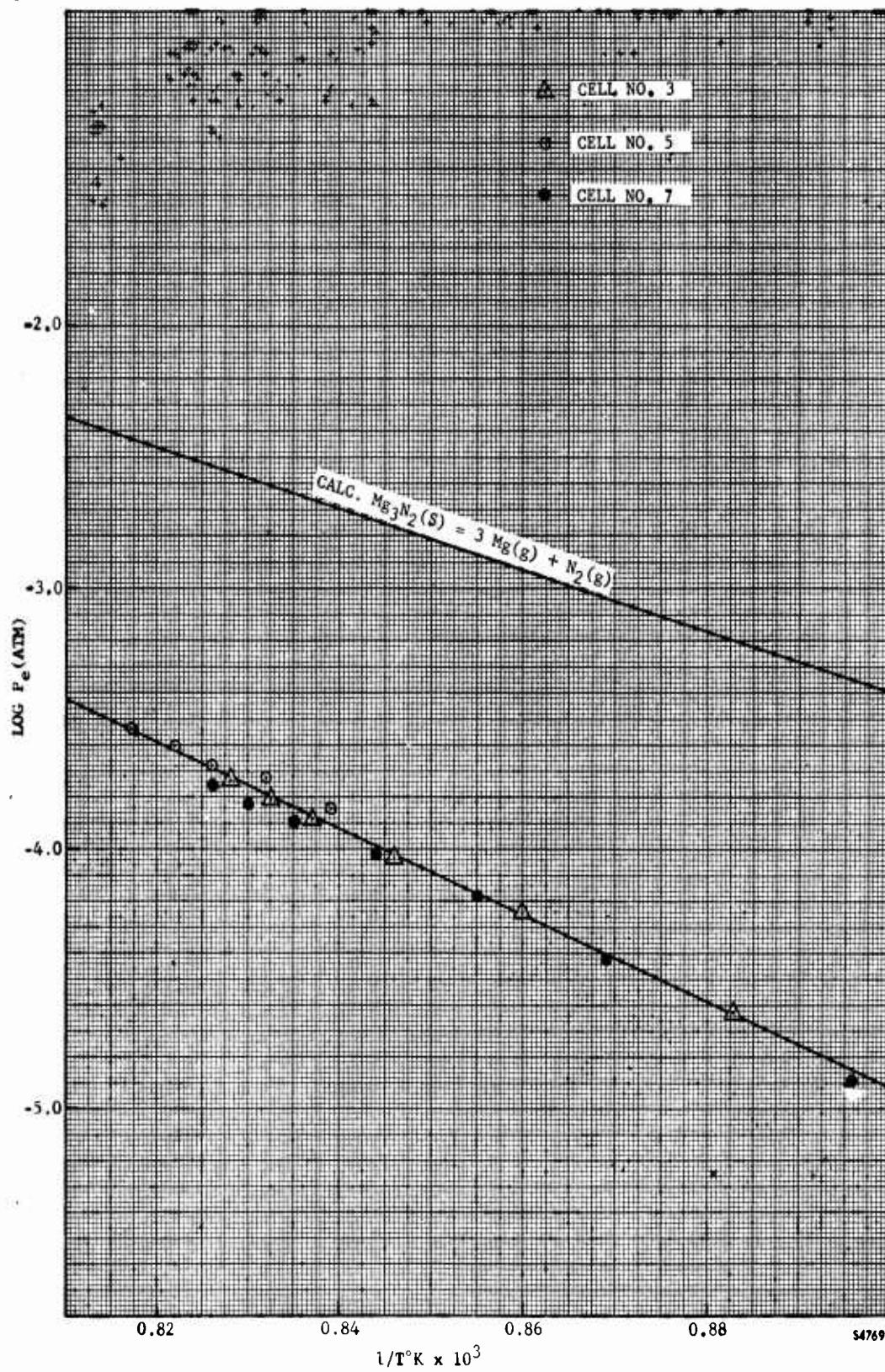


FIGURE 3. MAGNESIUM NITRIDE DISSOCIATION PRESSURE DATA

the results, the pressure measurements were repeated in the inductively-heated torsion apparatus¹, in which temperature measurement is made by optical pyrometry. The results obtained with the two different pieces of apparatus were in excellent agreement, indicating both temperature and pressure measurements to be substantially correct.

Of the possible errors in thermal data, only an error in the heat of formation of crystalline Mg₃N₂ is at all likely in accounting for the difference between experimental and calculated pressures. Even this value, however, seems well substantiated as -110.2 ± 1 kcal/mole¹³. A third law treatment of the derived "equilibrium" pressures in Table VI yields a ΔH_{298}^0 for reaction (8) of 243.5 ± 0.5 kcal/mole and a $\Delta H_f^0_{298}$ for Mg₃N₂(s) of -136 kcal/mole, the latter differing by 26 kcal/mole from the selected value. A second law treatment of the experimental pressures, however, leads to a ΔH_{298}^0 value for reaction (8) of 309 kcal/mole, 66 kcal higher than the third law value. The latter suggests that the vaporization does not proceed according to reaction (8), but, since no other process suggests itself, it appears that the vaporization must in some way be kinetically limited, and that the hole size correlation leads to "equilibrium" pressures that are much lower than the true values. Such an effect has been observed by Kay and Gregory¹⁴ in an effusion study of the vaporization of magnesium hydroxide. They observed an apparent low condensation coefficient from a smooth correlation of the data with equation (2), but the derived "equilibrium" pressures were lower than the well established true values by about 10⁴. This very large discrepancy was attributed to surface effects which severely limited the number of sites available for vaporization at the rate required by kinetic theory.

Soulen et al.¹⁵ have measured the dissociation pressure of Mg₃N₂ by the Knudsen effusion method, using MgO cells, and obtained pressures somewhat higher than those determined in this work, although still below the calculated pressures. However, their results contain too much scatter for a reasonable hole size correlation. Interestingly enough, the pressures of Soulen et al.¹⁵ also show a much larger temperature dependence than that calculated for reaction (8).

It is concluded that either the $\Delta H_f^0_{298}$ value for Mg₃N₂(s) is in error, or that the rate of vaporization is limited by a secondary process which leads to an apparently satisfactory but incorrect application of equation (2). At the moment, the latter possibility appears more likely.

AERONUTRONIC

AERONUTRONIC

A DIVISION OF *Ford Motor Company*

SECTION 3

TRANSPIRATION STUDIES

Flow studies on the reaction of elemental boron with boron trifluoride proved inconclusive regarding the stability of gaseous boron difluoride. The boron weight losses were too small to be considered significant, and would have been small even had appreciable reaction occurred. It is planned to study the reaction mass spectrometrically, in which case $\text{BF}_2(\text{g})$ can be readily detected if present at equilibrium. Contributions to the BF_2^+ peak from fragmentation of BF_3 can be separated out by means of a preliminary determination of the BF_3 cracking pattern.

Transpiration measurements on the $\text{ZrO}_2(\text{s}) + \text{HCl}(\text{g})$ reaction in the monel flow system have been limited because of corrosion problems a quartz flow system is being constructed for this purpose.



AERONUTRONIC

A DIVISION OF *Ford Motor Company*

SECTION 4

MASS SPECTROMETRY

4.1 VAPOR SPECIES IN THE BORON-OXYGEN-FLUORINE SYSTEM

The vapor effusing from a Knudsen cell containing a 1:1 mole ratio mixture of MgF_2 and B_2O_3 was examined mass spectrometrically.

The instrument used was a Nuclide Analysis Associates Model HT mass spectrometer, which is quite similar to the one described by Chupka and Inghram¹⁶. The sample was placed in a tungsten crucible (Knudsen cell) which was heated by electron bombardment and situated so that the effusing vapors streamed toward the electron bombardment ion source. All measurements were made at a cell temperature of 1268 °K. A travelling slit, called a shutter, separated the crucible and ion source compartments. The extent to which ion currents were due to vapors effusing from the crucible could be determined from a study of the effect of shutter position on ion intensities.

a. Results

Heights of important peaks in the mass spectrum are given in Table VII. Significant amounts of $(OBF)_3^+$, OBF^+ , BF_3^+ , BF_2^+ and B^+ were observed. Mass calibration was obtained with the aid of known peaks due to background mercury, air, water and hydrocarbons. Identities of the ions responsible for observed ion currents were determined from the mass numbers, the known composition of the sample, and the correlation between observed relative intensities and the known isotopic abundance ratio for the two naturally occurring stable isotopes of boron. For example, the intensity ratio of the peak at mass 11 to that at mass 10 is 4.1, which compares favorably with the $B^{11}:B^{10}$ natural abundance ratio 4.3. Similarly, the relative heights of the peaks at masses 135, 136, 137 and 138 approximate abundance ratios calculated for the random combination of three boron atoms in nature.

The last column of Table VII gives the effect of shutter movement on ion intensities. A positive shutter check indicates a significant, though not necessarily complete, reduction in intensity when the line of sight path between the effusion orifice and ion source is blocked. A partial check indicates a smaller, less pronounced reduction in intensity and a negative check indicates no noticeable change. Peaks corresponding to OBF^+ and $(\text{OBF})_2^+$ gave positive shutter checks, indicating that the molecular precursors of these ions originated within the crucible. BF_3^+ , BF_2^+ and B^+ all gave partial checks. Results of the shutter check on $(\text{OBF})_2^+$ were inconclusive due to the low intensities of the peaks and the presence of neighboring background peaks. CO_2^+ is included in the table to exhibit the negative effect of shutter position on background peaks.

b. Discussion

With metallic vapors and other highly condensable molecular beams one usually observes the virtual extinction of ion currents in a shutter check, provided there are no significant contributions to the ion currents by species produced from background gases. During the present experiments the instrument was in its initial testing period and had not yet been thoroughly baked out. As a result, background peaks appeared at nearly all neighboring masses with average intensities as high as 10 percent of the peaks of interest. It is therefore reasonable to expect that many of the peaks listed in Table VII contain significant contributions from background and that shutter checks in these instances cannot be expected to completely extinguish the ion currents. Incomplete suppression of ion currents in a shutter check might also be expected for permanent and semi-permanent gases effusing from the crucible at speeds in excess of the pumping speeds of the spectrometer diffusion pumps.

The molecular precursor of the $(\text{OBF})_3^+$ ion is probably the trimeric species $(\text{OBF})_3$. Production of the ion as a fragment from a larger molecule is unlikely, in view of the absence of detectable amounts of boron-containing ions at masses from m/e 139 to well beyond m/e 250. This conclusion is also supported by results of transpiration studies of the $\text{BF}_3 - \text{B}_2\text{O}_3$ reaction, performed in this laboratory, which indicate a high degree of stability for the $(\text{OBF})_3$ molecule. Similarly, the OBF^+ ion could be the result of direct ionization of monomeric OBF. However, with the relatively energetic electrons used to produce these spectra, the entire OBF^+ ion current could conceivably result from fragmentation of $(\text{OBF})_3$, despite the fact that the intensity of OBF^+ is four times that of $(\text{OBF})_3^+$. A combination of the two modes of formation seems likely. A more detailed investigation is expected to render a more definite conclusion in the near future.

AERONUTRONIC

AERONUTRONIC

A DIVISION OF *Ford Motor Company*

TABLE VII

MASS SPECTRUM OF VAPOR SPECIES FROM 1:1 MIXTURE
OF MgF_2 AND B_2O_3 AT $995^{\circ}C$

IONIZING ELECTRON ENERGY = 70 VOLTS

<u>m/e</u>	Peak Height <u>Chart Divisions</u>	Probable <u>Ion</u>	Total of <u>Isotopes</u>	Relative <u>Intensity</u>	<u>Shutter Check</u>
10	10.8	B^+	54.9	5.4	Partial
11	44.1				
44	753	CO_2^+			Negative
45	58.0	OBF^+	256	25.3	Positive
46	198				
48	191	BF_2^+	1013	100	Partial
49	822				
67	24.3	BF_3^+	103.3	10.2	Partial
68	79.0				
90	1.9				
91	7.0	$(OBF)_2^+$	18.2	1.8	Partial
92	9.3				
135	3.4				
136	8.4	$(OBF)_3^+$	62.6	6.2	Positive
137	22.1				
138	28.7				

AERONUTRONIC

AERONUTRONIC

DIVISION OF *Ford Motor Company*

The relative intensities of BF_3^+ and BF_2^+ agree, within a factor of two, with the corresponding values in the mass spectrum of boron trifluoride obtained by Marriott and Craggs¹⁷. Such agreement for two different instruments can be considered good. Since BF_3 is a permanent gas and since a high effusion pressure was used in order to exceed background, the existence of BF_3 as the precursor of BF_3^+ and BF_2^+ would explain the fact that these ions gave only partial shutter checks. Decomposition of $(\text{OBF})_3$ and OBF might be expected to produce BF_3 .

A detailed study of the reaction is planned. It is expected that a reliable value for the heat of formation of the gaseous OBF monomer can be obtained from a temperature study of the monomer-trimer equilibrium.



AERONUTRONIC

A DIVISION OF *Ford Motor Company*

SECTION 5

SPECIFIC HEAT MEASUREMENT

The applicability of the vacuum cooling rate method for specific heat measurement is being checked at temperatures below 1500 °K on materials whose specific heats are known. Measurements have been made on a solid tantalum cylinder and on a hollow platinum capsule (sample container). In both cases, the cooling rates were measured with thermocouples and the data evaluated from the relation

$$C = \frac{-\sigma A \epsilon (T^4 - T_0^4)}{m \frac{dT}{dt}}$$

where C is the specific heat, σ is the Stefan-Boltzmann constant, A and ϵ are the sample surface area and total emissivity, T and T_0 are the temperatures of the sample and the surroundings, m is the sample mass and dT/dt is the cooling rate. Surface areas were computed from the external dimensions of the samples and the emissivities were taken from the literature. Specific heats so determined were in good general agreement with literature values, although no attempt was made to obtain the most accurate values possible. The results were taken as an indication that the method is workable if certain conditions can be met.

Some additional measurements were made on a powdered aluminum oxide sample, using the platinum capsule sample container mentioned above. As expected with a poorly conducting powder, difficulty was experienced in achieving thermal equilibration within the sample. Attempts are being made to minimize the problem through use of a system of heat conducting vanes within the container and by cutting down the rate of cooling.

SECTION 6**FUTURE PROGRAM**

Vaporization studies on the LiF-AlF₃ system will be continued in order to establish the stability of other possible mixed metal fluoride species. Molecular weights of the AlF₃ and LiAlF₄ vapor species will be determined by weight loss measurements. The work will be extended to other mixed halide systems.

Mass spectrometric studies of the OBF gaseous monomer-trimer equilibrium will be continued. From the measured temperature dependence and the total pressure in the system determined from torsion measurements, it should be possible to establish a firm value for the heat of formation of the monomer.

A mass spectrometric study of the reaction of BF₃ with elemental boron will be made in order to fix the thermodynamic stability of gaseous BF₂.

Transpiration measurements will be carried out on the ZrO₂-HCl system in order to obtain information about vapor species. This will be followed up by a mass spectrometric investigation of the reaction.

It is planned to study the vaporization of Li₂O, B₂O₃ and their mixtures by the torsion method in order to reliably establish vapor thermal properties.

The mass spectrometer will be used to check the identity of vapor species in the nitride systems previously studied.

In the specific heat work, emphasis will be placed upon minimizing, if possible, the heat transfer problems associated with measurements on powdered samples.



AERONUTRONIC

A DIVISION OF *Ford Motor Company*

REFERENCES

1. "An Experimental Program for Obtaining the Thermodynamic Properties of Propellant Combustion Products", Contract NOrd 17980, Task 3, Aeronutronic Division of Ford Motor Co., Third Quarterly Report, Publication No. U-1187, 15 March 1961.
2. Ibid, Second Quarterly Report, Publication No. U-1085, 15 December 1960.
3. Ibid, First Quarterly Report, Publication No. U-985, 15 September 1960.
4. S. Cantor, R. F. Newton, W. R. Grimes and F. F. Blankenship, J. Phys. Chem., 62, 96 (1958).
5. K. A. Sense, M. J. Snyder and R. B. Filbert, J. Phys. Chem., 58, 995 (1954).
6. W. N. Hubbard, Argonne National Laboratory, Unpublished Result.
7. W. P. Witt and R. F. Barrow, Trans. Faraday Soc., 55, 730 (1959).
8. R. F. Porter and E. F. Zeller, J. Chem. Phys., 33, 858 (1960).
9. National Bureau of Standards Report No. 6928, 1 July 1960.
10. National Bureau of Standards Report No. 6484, 1 July 1959.
11. J. P. Coughlin, J. Am. Chem. Soc., 80, 1802 (1958).
12. D. W. Mitchell, Ind. Eng. Chem., 41, 2027 (1949).
13. National Bureau of Standards Report No. 6645, 1 April 1960.
14. E. Kay and N. W. Gregory, J. Phys. Chem., 62, 1079 (1958).
15. J. R. Soulen, P. Sthapitanonda and J. L. Margrave, J. Phys. Chem., 59, 132 (1955).
16. W. A. Chupka and M. G. Inghram, J. Phys. Chem., 59, 100 (1955).
17. J. Marriott and J. D. Craggs, J. Electronics and Control, 3, 194 (1957).



AERONUTRONIC

A DIVISION OF Ford Motor Company

JANAF/SPIA DISTRIBUTION LIST

15 MAY 1961

Director
Advanced Research Projects Agency
The Pentagon, Room 3D154
Washington 25, D.C.

Attn: Fred A. Koether
Tech. Info. Office

D-1
4 Copies

Commander
Armed Services Tech. Information
Agency
Arlington Hall Station
Arlington 12, Virginia

Attn: TIPCR

AF-12
10 Copies

U.S. Dept of the Interior
Bureau of Mines
4300 Forbes Street
Pittsburgh 13, Pennsylvania

Attn: M.P. Benoy, Rpts Librarian
Explosives Research Lab

D-2
1 Copy

Commander
Wright Air Development Division
Wright-Patterson Air Force Base
Ohio

Attn: WWRCNP

AF-15
1 Copy

National Aeronautics and
Space Administration
1520 H Street, N.W.
Washington 25, D.C.

Attn: Launch Propulsion

D-3
7 Copies

Commanding General
Aberdeen Proving Ground
Maryland

Attn: Ballistic Research Lab

A-1
1 Copy

Commander
Air Force Flight Test Center
Edwards Air Force Base
California

Attn: FTRS

AF-4
1 Copy

Commander
Army Rocket and Guided Missile Agency
Redstone Arsenal
Alabama

Attn: Technical Library

A-11
4 Copies



AERONUTRONIC

AERONUTRONIC

A DIVISION OF *Ford Motor Company*

JANAF/SPIA DISTRIBUTION LIST (Continued)

Commander
Air Force Ballistic Missile Division
Hq, Air Res. and Dev. Command
P.O. Box 262
Inglewood, California

Attn: WDAT

AF-11
1 Copy

Commander
Army Ballistic Missile Agency
Redstone Arsenal, Alabama

Attn: ORDAB-HSI

A-21
1 Copy

Bureau of Naval Weapons
Department of the Navy
Washington 25, D.C.

Attn: DLI-3

N-2
2 Copies

Department of the Navy
Office of Naval Research
Washington 25, D.C.

Attn: Code 426

N-12
1 Copy

Bureau of Naval Weapons
Department of the Navy
Washington 25, D.C.

Attn: RMMP-2

N-3
2 Copies

Special Projects Office
Department of the Navy
Washington 25, D.C.

Attn: SP-271

N-18
1 Copy

Bureau of Naval Weapons
Department of the Navy
Washington 25, D.C.

Attn: RMMP-331

N-4
1 Copy

U.S. Naval Ordnance Laboratory
Corona
California

Attn: B.K.W. Bartocha

N-22
1 Copy



AERONUTRONIC

AERONUTRONIC

A DIVISION OF *Ford Motor Company*

• JANAF/SPLA DISTRIBUTION LIST (Continued)

Commanding Officer
U.S. Naval Propellant Plant
Indian Head, Maryland

Aerojet-General Corp.
P.O. Box 296
Azusa, California

Attn: Research and Development
Department

N-7
2 Copies

Attn: Librarian

C-1
3 Copies

Commander
U.S. Naval Ordnance Laboratory
White Oak
Silver Spring, Maryland

Hercules Powder Company
Allegany Ballistics Laboratory
P.O. Box 210
Cumberland, Maryland

Attn: Library

N-9
1 Copy

Attn: Library

C-2
3 Copies

Commander
U.S. Naval Ordnance Test Station
China Lake, California

Atlantic Research Corp
Shirley Highway and Edsall Road
Alexandria, Virginia

Attn: Tech. Library
Branch

N-10
1 Copy

C-5
1 Copy

Texaco Experiment Incorporated
P.O. Box 1-T
Richmond 2, Virginia

Olin Mathieson Chemical Corporation
Marion, Illinois

C-14
1 Copy

Attn: Research Library
Box 508

C-43
1 Copy

Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena 3, California

Reaction Motors Division
Thiokol Chemical Corporation
Denville, New Jersey

Attn: I.E. Newlan, Chief
Reports Group

C-20
1 Copy

Attn: Librarian

C-44
1 Copy



AERONUTRONIC

A DIVISION OF *Ford Motor Company*

JANAF/SPIA DISTRIBUTION LIST (Continued)

Rohm and Haas Company
Redstone Arsenal Research Div.
Huntsville, Alabama

Attn: Librarian

C-36
2 Copies

Rocketdyne, A Division of
North American Aviation Inc.
Solid Propulsion Operations
P.O. Box 548

McGregor, Texas

Attn: Library

C-49
1 Copy

Solid Propellant Information
Agency
The Johns Hopkins University
Silver Spring, Maryland

C-37
3 Copies

Department of Chemical Engineering
New York University
New York 53, New York

Attn: C.J. Marsel

C-57
1 Copy

Thiokol Chemical Corporation
Redstone Division
Huntsville, Alabama

Attn: Technical Director

C-39
2 Copies

Rocketdyne
6633 Canoga Avenue
Canoga Park, California

Attn: Library
Dept. 596-306

C-61
3 Copies

Thiokol Chemical Corporation
Elkton Division
Elkton, Maryland

Attn: Librarian

C-41
1 Copy

Grand Central Rocket Company
P.O. Box 111
Redlands, California

Attn: Helen Ashman
Librarian

C-65
3 Copies

AERONUTRONIC

AERONUTRONIC

A DIVISION OF *Ford Motor Company*

JANAF/SPIA DISTRIBUTION LIST (Continued)

Aerojet-General Corporation
Box 1168
Sacramento, California

Attn: R.G. Weitz, Head
Tech Info Center

C-72
3 Copies

American Cyanamid Company
1937 W. Main Street
Stamford, Connecticut

Attn: Dr. A.L. Peiker

C-96
1 Copy

Olin Mathieson Chemical Corporation
Research Library 1-K-3
275 Winchester Avenue
New Haven, Connecticut

Attn: Mail Control Room
Miss Laura M. Kajuti

C-76
3 Copies

Hercules Powder Company
Bacchus Works
Magna, Utah

Attn: Librarian

C-98
1 Copy

Ethyl Corporation
Research Laboratories
1600 West Eight Mile Road
Ferndale, Michigan

Attn: E.B. Rifkin, Asst. Dir.
Chemical Research

C-90
1 Copy

Allied Chemical Corporation
General Chemical Division
Research Laboratory
P.O. Box 405
Morristown, New Jersey

Attn: H.R. Neumark

C-106
1 Copy

The Dow Chemical Company
Midland, Michigan

Attn: Harold A. Robinson
Technical Director,
644 Building

C-91
1 Copy

General Electric Company
Cincinnati 15, Ohio

Attn: Tech Info Center

C-107
1 Copy

AERONUTRONIC

AERONUTRONIC

A DIVISION OF *Ford Motor Company*

JANAF/SPIA DISTRIBUTION LIST (Continued)

Minnesota Mining and Manufacturing Co.
900 Bush Avenue.
St. Paul 6, Minnesota

Attn: J.W. Millin

C-94
2 Copies

VIA. R.W. McElroy
Security Administrator

Callery Chemical Company
Research and Development
Callery, Pennsylvania

Attn: Document Control

C-112
1 Copy

Pennsalt Chemicals Corporation
Box 4383
Philadelphia 18, Pennsylvania

Attn: Dr. G. Barth-Wehrenalp C-114
1 Copy

The B.F. Goodrich Company
Research Center
Brecksville, Ohio

Attn: Charles H. Stockman

C-113
1 Copy

Defence Research Member
Canadian Joint Staff (W)
2450 Massachusetts Avenue, N.W.
Washington 8, D.C.

F-2
4 Copies

VIA: Chief, Bureau of Naval Weapons
Department of the Navy
Washington 25, D.C.

Attn: DSC-3

AERONUTRONIC

AERONUTRONIC

A DIVISION OF *Ford Motor Company*

JANAF/SPIA DISTRIBUTION LIST (Continued)

Space Technology Laboratory, Inc.
5730 Arbor-Vitae Street
Los Angeles 45, California

Attn: Mr. Robert C. Anderson C-116
1 Copy

J. I. Thompson and Company
1118 22nd Street, N.W.
Washington 25, D.C.

Attn: Mr. K. Dahl-Hansen 1 Copy

VIA: U.S. Bureau of Naval Weapons Resident
Representative
Applied Physics Laboratory
Silver Spring, Maryland

Union Carbide Corporation
270 Park Avenue
New York 17, New York

Attn: B.J. Miller

C-121
1 Copy

Aerospace Corporation
P.O. Box 95085
Los Angeles 45, California

Attn: Technical Information C-129
Center
Acquisitions 2 Copies

United Technology Corp.
P.O. Box 358
Sunnyvale, California

Attn: Librarian

C-124
1 Copy

British Defence Staff
British Embassy
3100 Massachusetts Avenue
Washington, D.C.

Attn: Scientific Information Officer F-1
4 Copies

VIA: Chief, Bureau of Naval Weapons
Department of the Navy
Washington 25, D.C.

Attn: DSC-3

LETTER REQUEST DISTRIBUTION

Dr. Robert Freeman Assoc. Professor of Chemistry Oklahoma State University Stillwater, Oklahoma	1 copy	Bureau of Naval Weapons Department of the Navy Washington 25, D.C. Attn: RMMP-221	2 copies
Mr. J. J. Wittlebort, WWRCP Chief, Thermophysics Branch Materials Control Wright Air Development Division Wright-Patterson Air Force Base Ohio	1 copy	Mr. H. Bartick Code WCL PPFF Fuels and Oils Branch Bldg. 70, Area B Wright Air Development Division Wright-Patterson Air Force Base Ohio	1 copy
Dr. Daniel R. Stull Thermal Laboratory Building #574 The Dow Chemical Co. Midland, Michigan	1 copy	AVCO Corporation Research and Advanced Development Division 201 Lowell Street Wilmington, Mass. Attn: Dr. H. L. Schick	1 copy
Dr. C. W. Beckett Head Division 107 West Bldg. National Bureau of Standards Washington 25, D.C.	2 copies		
Prof. Paul W. Gilles Department of Chemistry University of Kansas Lawrence, Kansas	1 copy		
Also: Advanced Research Projects Agency The Pentagon Room 3D154 Washington 25, D.C. Attn: T.O. Dobbin Dr. W. H. Jones	1 copy 1 copy		

UNCLASSIFIED

UNCLASSIFIED